Saathi

Date 01 / 03 / 2016

Unit - 1
The Solid State

The State of matter which have definate shape, size volume & have rigidity is known as solid state
Ex- Table, chair, etc.

Properties of solid
→ They have definate shape, size and volume.
→ They have max^m inter molecular force of attraction
→ They have min^m inter molecular space.
→ They have rigidity due to max^m inter molecular force of attraction

Types of solid

- solid
  - Amorphus
  - crystalline
    - Ionic
    - covalent
    - Metallic
    - Molecular
      - Polar
      - Non-Polar
      - H-bonding

Amorphus - Those solid which have irregular arrangement of particles for long range order are known as amorphus
Ex- polythene, PVC, rubber, etc.

Properties of Amorphus
→ They have irregular arrangement of particle
→ They have rough surface when cut with sharp tool
→ They have indefinate enthalpy of fusion and vapourisation.
→ They do not have Fixed MP & BP. They are isotropic in Nature.

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Isotropic Nature :- when physical property of solid like Refractive index, magnetic behaviour remain same when observe from diff. direction Then it is called Isotropic Nature

Ex- Amorphus Solid.

NOTE.
- Glass is consider as a super cooled because it have flowing property which flow from higher level to lower level. old glass become milky due to anaelization.
- Amorphus solid considered as pseudo solid Because they do not have property of solid.

Crystalline solid - Those solid which have regular arrangement of particle for long range order are known as crystalline

Ex- Ice, Gold, platineum

Properties of crystalline :-

1- They have regular arrangement of particle for long range order.

2- They form smooth surface when cut with the sharp tool.

3- They have fixed Enthalpy of fusion + vapourisation

4- They have sharp MP + BP

5- They are anisotropic in nature

6- They are true solid.

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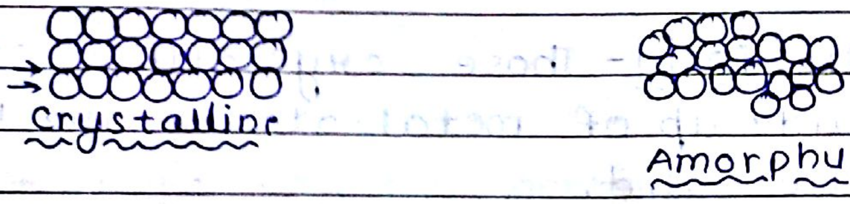
Anisotrophic Nature → when physical property like Refractive index, Magnetic Behaviour do not remains same when they observe from different direction then it is called Anisotrophic Nature

Ex- crystalline solid



Types of crystalline solid:-

① Ionic solid - Those solid which are made up of cation & Anion

Properties

→ constituent particle - cation & Anion
→ Force of Attraction - Electrostatic
→ Bonding - Ionic & Electrovalent
→ conductivity - Bad (solid) Good (Liquid/Molten)
→ MP & BP - high
→ Nature - Brittle solid

Example - NaCl, AgBr, AgCl, AgI

② covalent or Network solid:- Those solid which are made up of covalent bond in form of large Network are known as covalent solid.

Properties

→ constituent Particle - Atoms
→ Force of Attraction - None
→ Bonding - covalent
→ conductivity - Bad (Except graphite)

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→ MP & BP - very high
→ Density - high
→ Nature - Brittle solid & hard

Ex- Diamond, Graphite, Fullerence, Silicons, Silicon carbide (SiC), silica (SiO_2)

③ Metallic Solid - Those crystalline solid which are made up of metal atoms are known as Metallic Solid.

Properties
→ constituent particle - Metal atoms or kernel's & Electron Pool
→ Force of Attraction - Electrostatic
→ Bonding - Metallic Bonding
→ conductivity - Good (Except Lead)
→ MP & BP - High
→ Nature - Melleable, Ductile, sonorous, lusterous

Example - Ag, Au, Pt, Na, K, Fe, Co, Ni, etc

④ Molecular Solid - Those crystalline solid which made by the molecules. There are 3 types of molecular solids.

	Polar	Non-Polar	H-Bonding
constituent Particles :-	Polar Molecule	Non-Polar molecule	Molecules having H-Bonding
Force of attraction :-	DP - DP	London Force	Specific DP FON / H

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Bonding:-	vanderwall	vanderwall	H-Bonding
conductivity:-	Bad	Bad	Bad
MP & BP	Moderate	Low	high
Nature	Mostly Liquid	Gas	Liquid

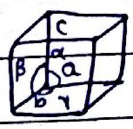
Unit cell - The smallest portion of crystalattice which repeated over & again in different direction to form complete lattice is known as unit cell.

crystalattice - 3D arrangement of particle in solid is known as crystalattice.

There are 7 types of crystal system

1. cubic
2. Rhombohedral
3. orthorhombic
4. Triclinic
5. Monoclinic
6. Tetragonal
7. Hexagonal

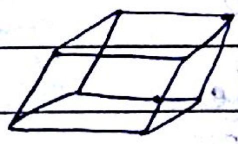
(1)



$a = b = c$

$\alpha = \beta = \gamma = 90°$

(2)



$a = b = c$

$\alpha = \beta = \gamma \neq 90°$

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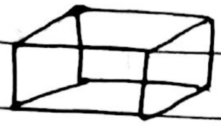
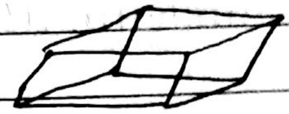
(3)



$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

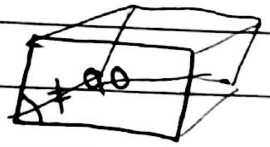
(4)



$a \neq b \neq c$

$\alpha = \beta = \gamma \neq 90$

(5)

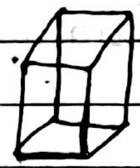


$a \neq b \neq c$

$\alpha = \gamma = 90°$

$\beta \neq 90°$

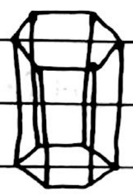
(6)



$a = b \neq c$

$\alpha = \beta = \gamma = 90°$

(7)



$a = b \neq c$

$\alpha = \beta = 90°$

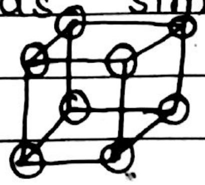
$\gamma = 120°$

Types of unit cell - It is of 2 types

(1) Primitive or simple

(2) centered.

(1) when particles arrange at the corner of unit cell then it is called primitive unit cell. It is also known as simple unit cell.



simple

cubic

centred

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(2) In this type of unit cell particles arrange at the corner as well as other side like body center, phase center, etc.

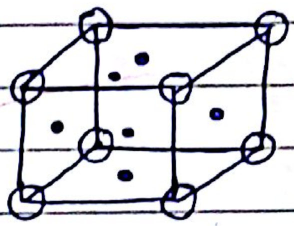
There are three types of centred unit cell.

(i) Face centered cube.

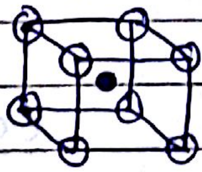
(ii) Body centered cube.

(iii) End phase centered cube.

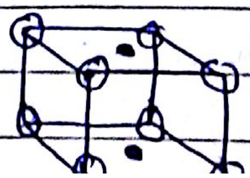
(i) Face centered cube - when particles arrange at the corners as well as center of each face then it is called FCC



Body centered cube - In this type of unit cell particles arrange at the corners as well as centeres of body of the unit cell



End phase centered cube - In this type of unit cell particle arrange at the corner as well as center of two opposite phase.



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calculation of no. of particles per unit cell.

SCC

corner = 8

contribution - $\frac{1}{8}$

$= \cancel{8} \times \frac{1}{\cancel{8}} = 1$

FCC

corner = 8

contribution = $\frac{1}{8}$

$= 8 \times \frac{1}{8}$

$= 1$

face = 6

cont. = $\frac{1}{2}$

$= 6 \times \frac{1}{2}$

$= 3$

Total $1 + 3 = 4$

BCC

corner = 8

contri. = $\frac{1}{8}$

$= 8 \times \frac{1}{8} = 1$

body centre = 1

Total = $1 + 1 = 2$

① lattice Point

	Ptr
corner	- 8
edge	- 12
face	- 6
Body centre	- 1
Body diagonal	- 4

② contribution

corner	- 1/8
edge	- 1/4
face	- 1/2
Body centre	- 1
Body diagonal	- 1

(z)

SCC	-	1
FCC	-	4
BCC	-	2
ECC	-	2
HCP	-	6

ECC. corner = 8

contribution = $\frac{1}{8}$

$= 8 \times \frac{1}{8} = 1$

face = 2

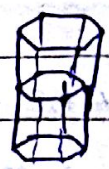
contri. = $\frac{1}{2}$

$= \cancel{2} \times \frac{1}{\cancel{2}} = 1$

$= 1 + 1 = 2$

HCP

corner $= 12 \times \frac{1}{4} = 3$



face $= 6 \times \frac{1}{2} = 3$

$= 6$

Q1 AB

A = corner

B = centre of face of cube

A	B
corner	face
$8 \times \frac{1}{8}$	$6 \times \frac{1}{2}$
$= 1$	$= 3$

AB_3

Q2 PQ

P = corner (−2)

Q = 4 face

P	Q
$6 \times \frac{1}{8}$	$4 \times \frac{1}{2}$
$\frac{3}{4}$	2

$P_{\frac{3}{4}} Q_2$

$P_3 Q_8$

Packing efficiency - space occupy by the particle in the crystal is known as packing efficiency

from the figure

$a = 2r$

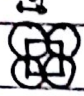
vol. of cube $= a^3$

$= (2r)^3$

$= 8r^3$

vol. of sphere $= \frac{4}{3}\pi r^3$

$Pe\% = \frac{\text{vol. of all sp.}}{\text{vol. of cube}} \times 100$



Ia

a = edge of crystal

$Pe\% = \frac{\cancel{4}\pi \cancel{r^3} \times 100}{3 \times \cancel{8} \cancel{r^3}}$

$= \frac{\overset{11}{\cancel{22}} \times 100}{7 \times 3 \times \cancel{2}} = \frac{1100}{21}$

$= 52.3\%$

Total no. of particle per unit cell $= 1$ (2)

∴ Total volume of all sphere $= 2 \times \frac{4}{3}\pi r^3$

$= \frac{4}{3}\pi r^3$

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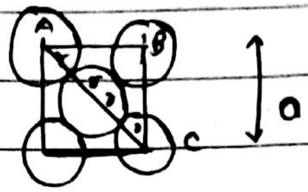
Face centred cube



from ΔABC

$(AC)^2 = AB^2 + BC^2$

$= a^2 + a^2$

$(AC)^2 = 2a^2$

$AC = \sqrt{2}\ a$

$\because AC = 4r$

$4r = \sqrt{2}\ a$

$a = 4r/\sqrt{2}$

vol. of cube $= a^3$

$= \left(\frac{4r}{\sqrt{2}}\right)^3$

$= \frac{64r^3}{2\sqrt{2}}$

vol. of sphere $= \frac{4}{3}\pi r^3$

Total No. of particle per unit cell = 4
(z)

Total vol. of all sphere $= z \times \frac{4}{3}\pi r^3$

$= 4 \times \frac{4}{3}\pi r^3$

$Pe\% = \frac{\text{vol. of all sp.}}{\text{volume of cube}} \times 100$

$Pe\% = \frac{4 \times 4 \times 22 r^3 \times 100 \times 2\sqrt{2}}{3 \times 7 \times 64 r^3}$

$= \frac{11 \times 1.414 \times 100}{21}$

$= 74\%$

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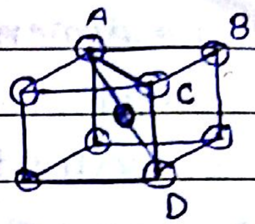
Body centered cube

From $\triangle ABC$

$AC^2 = AB^2 + BC^2$

$= a^2 + a^2$

$(AC)^2 = 2a^2$



from $\triangle ACD$

$(AD)^2 = AC^2 + CD^2$

$= 2a^2 + a^2$

$AD^2 = 3a^2$

$AD = \sqrt{3}\, a$

$\because AD = 4r$

$4r = \sqrt{3}\, a$

$a = \frac{4r}{\sqrt{3}}$

$Pe\,\% = \frac{\text{vol. of all sphere}}{\text{vol. of cube}} \times 100$

$= 2 \times \frac{4}{3} \times \frac{22}{7} r^3 \times 100 \times \frac{3\sqrt{3}}{64 r^3}$

$= \frac{11 \times 100 \times 1.732}{7 \times 4}$

$= 68\,\%$

volume of cube $= a^3$

$= \left(\frac{4r}{\sqrt{3}}\right)^3$

$= \frac{64 r^3}{3\sqrt{3}}$

vol. of sphere $= \frac{4}{3}\pi r^3$

No. of particles per unit cell $(z) = 2$

Total volume of all sphere $= 2 \times \frac{4}{3}\pi r^3$

$= 2 \times \frac{4}{3}\pi r^3$

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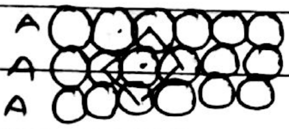
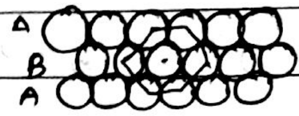
close packing

① one dimension - In this type of arrangement particle arrange in linear fashion having cordination no. 2

② Two dimension-





AAA

square close packing
coordination no. -4

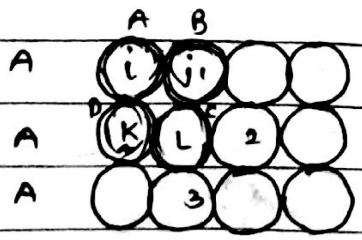
Hexagonal close packing
coordination no. 6

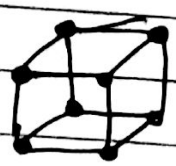
Square close packing - when second layer particle arrange just above the particles of first layer then they form AAA pattern in square close packing. having coordination number 4

Hexagonal close packing - when second layer particle arrange in the depression of Ist layer then they form ABA pattern in Hexagonal close packing. having cordination no. 6

③ Three dimension:-

square close packing in 3D →





scc

coordination no. -6

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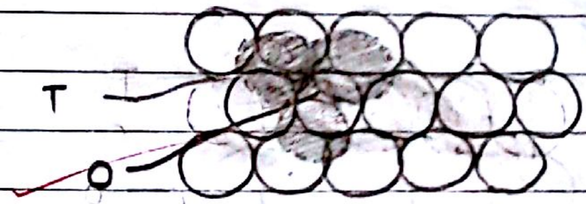
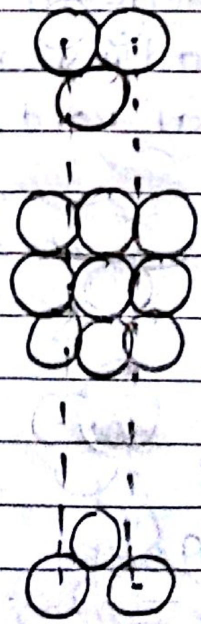
when particles of Ist layer arrange just above the particles of IInd layer in all direction then they have same alignment hence they form AAA pattern in simple cubic crystal having coordination no. 6

Hexagonal close packing :- In this type of arrangement particles of IInd layer arrange in the depression of Ist layer. In which IIIrd layer arrangement determine type of crystal



(A) when IIIrd layer particle occupy tetrahedral void of IInd layer then they form ABA pattern in Hexagonal close packing Having coordination Number 12



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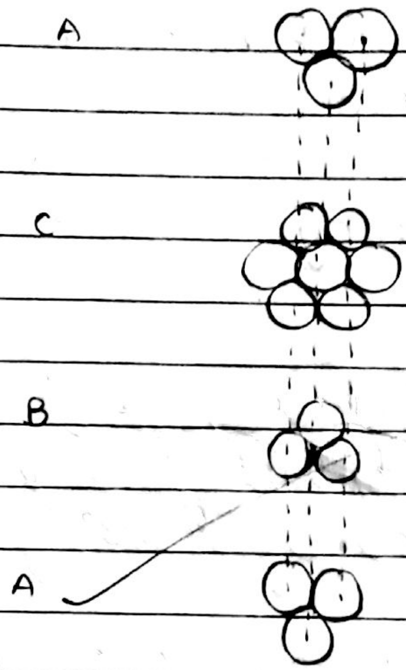
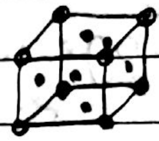
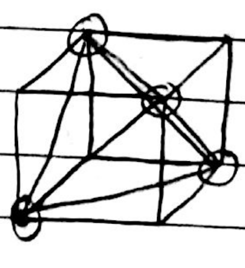
(B) When III^{rd} layer particle occupy octahederal void of second layer then they form ABCA pattern in cubic close packing [CCP] or face centered cube [FCC] crystal structure having coordination number - 12



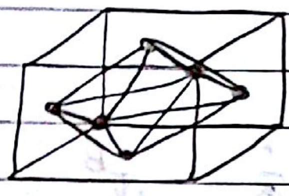


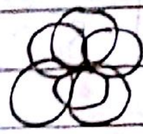
Tetrahederal void - The void which occurs in tetrahederal shape having coordination no. 4 and radius ratio 0.225 is known as Tetra hederal void.

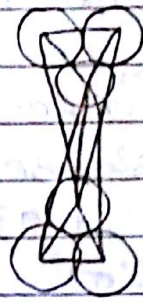


octahederal void

The void which occurs in octahedral shape having coordination no. 6 & radius ratio 0.414 is known as octahederal void



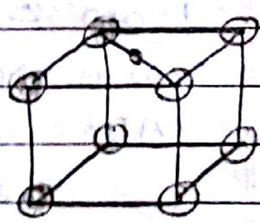


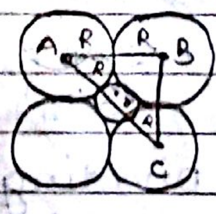


calculation of radius ratio-

① octahedral radius ratio-

from the fig





$\triangle ABC$

$AC^2 = AB^2 + BC^2$

$= a^2 + a^2$

$(AC)^2 = 2a^2$

$AC = \sqrt{2}\, a$

$\because AC = 2(r+R)$

$2(r+R) = \sqrt{2}\, a$ ----(i)

$\because AB = a$

& $AB = 2R$

$2R = a$ ------ (ii)

$r = r^+$

$R = r^-$

Div. eqn ① by ②

$$\frac{2(R+r)}{2R} = \frac{\sqrt{2}\,\cancel{a}}{\cancel{a}}$$

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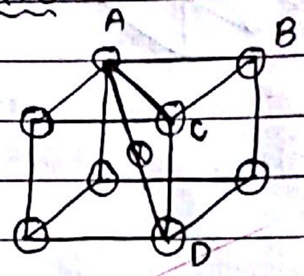
$$\frac{r}{R} + \frac{R}{R} = \sqrt{2}$$

$$\frac{r}{R} = 1.414 - 1$$

$$\boxed{\frac{r}{R} = 0.414}$$

② Tetrahedral radius ratio -



from $\triangle ABC$

$AC^2 = AB^2 + BC^2$

$= a^2 + a^2$

$AC^2 = 2a^2$

$AC = \sqrt{2}\, a$

$\because AC = 2R$

$2R = \sqrt{2}\, a$ - - - - (i)

from $\triangle ACD$

$AD^2 = AC^2 + CD^2$

$AD^2 = 2a^2 + a^2$

$= 3a^2$

$AD = \sqrt{3}a$

$\because AD = 2(r+R)$

$2(r+R) = \sqrt{3}\, a$ - - -(ii)

Dividing eq. (ii) by eq. (i)

$$\frac{\cancel{2}(r+R)}{\cancel{2}R} = \frac{\sqrt{3}\cancel{a}}{\sqrt{2}\cancel{a}}$$

$$\frac{r}{R} + \frac{R}{R} = \frac{\sqrt{3}}{\sqrt{2}}$$

$$\frac{r}{R} = \frac{\sqrt{3}}{\sqrt{2}} - 1$$

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$$\frac{r}{R} = \frac{1.732 - 1.414}{1.414}$$

$$\frac{r}{R} = 0.225$$

$$\boxed{r^+ = 0.225\, r^-}$$

$r = r^+$

$R = r^-$

Table:

S.No.	Radius Ratio	co-ordination number	Type of void.	Example
1 -	0.155 - 0.255	3	Trigonal	B_2O_3
2 -	0.225 - 0.414	4	Tetrahedral	ZnS
3 -	0.414 - 0.732	6	octahedral	NaCl
4 -	0.732 - 1.00	8	BCC	CsCl

→ calculation of density of crystal.

let the edge of crystal be a, volume $= a^3$, mass of particle $= w$, Atomic mass $= A$, Avogadro No. $= N_A$ Than

Volume of cube $= a^3$

No. of atom $= \frac{w}{A} \times N_A$

mass of 1 particle $= \frac{A}{N_A}$

No. of Atom per unit cell $= Z$

Mass of total atom $= \frac{ZA}{N_A}$

density $= \frac{mass}{volume}$

$$\rho = \frac{ZA}{N_A a^3}$$

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Defect or imperfection in solid : Irregularities or disordering in the arrangement of particle of solid is known as Defect or Imperfection.

Types of Defect -

There are 2 types of defect

1. Point defect
2. Line defect

(1) When disordering in the arrangement of particle takes place in a point then it is called point defect. It is of 3 types

1. stoichiometric defect
2. Non-stoichiometric "
3. impurity

(1) stoichiometric - when disordering in the particles of crystal takes place in a point in which stoichiometry or ratio of cation & anion remain same. There are 4 types of stoichiometric defect.

(i) shottky defect
(ii) Frankel defect
(iii) vacancy "
(iv) Interstitial "

(i) shottky defect → This type of defect arise in those ionic crystal which have approx similar size of cation & Anion. In this defect equal no. of cation & Anion leave crystal hence decrease the density of crystal.

Ex - $NaCl$, $NaBr$, NaI, $AgBr$

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(ii) Frankel defect - This defect arise in those ionic crystal which have difference in size of cation and Anion. In this defect small size ion (mostly cation) misplace their position & occupy Interstecial site. Hence No, change in density takes place.

Ex- AgCl, AgBr, AgI, ZnS, etc

(iii) Vacancy defect - This defect arise in non-ionic crystal in which particles leave the crystal to decrease density.

Ex- Iodine

(iv) Interstitial defect - This defect occurs in non-ionic crystal in which any small foreign particle occupy interstecial site hence increase the density of crystal.

Ex - Fe, Co, Ni

(2) Non-stoichiometric defect → This defect ratio of cation & Anion does not remains same hence it is called Non-stoichiometric defect. It is of two types -

(i) Metal Excess defect.

(ii) Metal deficient defect.

A (i) Metal Excess defect → When any Ionic crystal heated in the metal vapour of its own Then metal vapour take anion along with it and create vacancy. This anionic vacancy occupied by the electron which is called F-center (Farbenzenter). It is called metal Excess defect. This F-centre responcible

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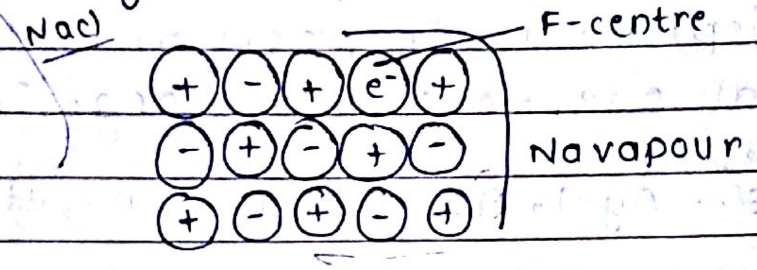
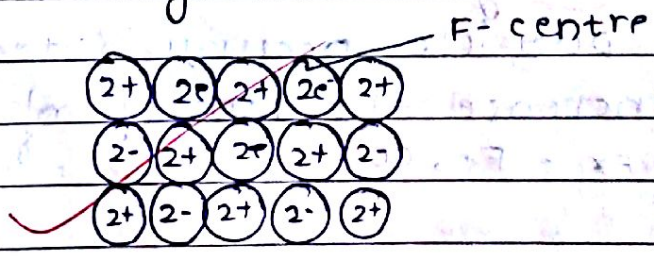
for the colour of crystal

For Ex- When NaCl heated with sodium vapour it gives yellow colour.



$$Na \rightarrow Na^+ + e^-$$

3) (i) when zinc oxide heated at high temperature then it librate oxygen gas & this anionic vacancy occupied by electron hence, it show Yellow colour of the crystal.



$$ZnO \longrightarrow Zn^{2+} + \frac{1}{2} O_2 + 2e^-$$

(ii) Metal deficient defect - when oxide of transition element heated then metal ion leave the crystal by increasing oxidation number of remaining metal atom to maintain electrical neutrality. This is called Metal deficient defect.

Ex- $Ni_{0.96}O_{1.00}$

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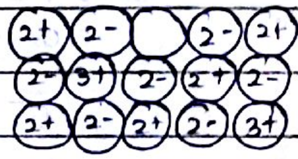
Q. calculate Fe^{2+} and Fe^{3+} ion in $Fe_{0.98}O_{1.00}$ crystal?

→ let the Fe^{2+} ions are $= x$

$Fe^{3+} = 0.98 - x$

$O^{2-} = 1.00$



$Fe_{0.98}O_{1.00}$

$(+)ve = (-)ve$

$2x + 3(0.98 - x) = 2(1.00)$

$2x + 2.94 - 3x = 2$

$2.94 - x = 2$

$x = 2.94 - 2$

$\boxed{x = 0.94}$

$Fe^{2+} = 0.94$

$Fe^{3+} = 0.98 - 0.94$

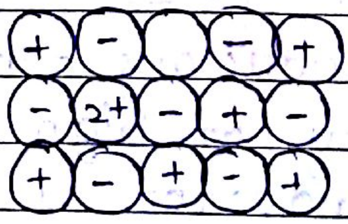
$= 0.04$

③ Impurity defect - This defect arise by the doping of Impurity in the ionic crystal having less oxidation Number.

For ex- $SrCl_2$ doped in the NaCl crystal in which one Sr ion displace two sodium ion in which Sr occupy one cationic vacancy & another cationic vacancy remain vacant hence no. of vacant space are equal to the doped molecule.

(+) $= Na^+$

(−) $= Cl^-$



$SrCl_2 | Sr^{2+}$

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Q. calculate vacant space in the NaCl crystal when 10^{-3} mole % $SrCl_2$ doped in it.

→ 10^{-3} %

$= \frac{10^{-3}}{100}$ mol

$= 10^{-5}$ mol

$= 10^{-5} \times 6.02 \times 10^{23}$

$= 6.023 \times 10^{18}$ vacant space

② Line defect - when irregularity in the arrangement of particles takes place in entire row then it is called line defect or row defect.

★ CONDUCTORS

(i) Good conductors - Those substance which allow Electricity to pass through them. They have conductivity range 10^4 to 10^7 S cm^{-1}

Ex - Ag, Au, Cu, Fe, Co, Ni

(ii) Bad conductors :- Those substance which do not allow electricity to pass through them are known as Bad conductors. These have conductivity range 10^{-22} to 10^{-10} S cm^{-1}

Ex - PVC, plastic, etc.

(iii) Semi-conductors - Those substance which conduct electricity at high temp. but behave like bad conductor at low temp. are known semi-conductor. These have conductivity range from 10^{-6} to 10^4 S cm^{-1}

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It is of two types
(i) Intrinsic semi- conductor
(ii) Extrinsic " "

(i) It is the purest form of semi conductors which is made up of only single type of atom
Ex - Ge, Ga, Si

(ii) This type of semi-conductor is form by the doping of Impurity in the Intrinsic semi-conductor-s

There are two types of Extrinsic semi-conductors
① n- type
② p- type

(i) n-type - This type of semi conductor form by the mixing of 15 group element in 14 group element. Hence they have free e^- which help in conduction of electricity.
Ex - As + Si

(ii) p-type - This type of semi-conductor form by the mixing of 13 group impurity in 14 group elements. Hence positive hole help in the conduction of electricity
Ex - Ga + Si

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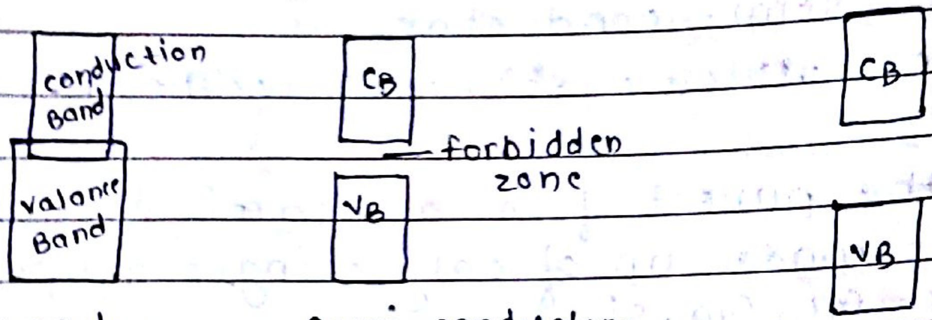
Band theory:



Good   Semi-conductors   Insulators

- Good conductors have no dist. b/w V_B & C_B Therefore they conduct electricity at all temp.
- Semi conductors have less forbidden zone between V_B & C_B. Therefore they behave like insulator at low temp. and good conductor at high temp.
- Bad conductors have large gap between V_B & C_B hence electron can't jump from V_B to C_B.

Magnetic Mo_ment

Magnetic Behaviour of any solid is due to the Electron spin & revolution which is responsible for the domance. There are 5 types of magnetic property shown by solid.

① **Paramagnetic** - This type of Magnetic Behaviour occurs due to the presence of unpaired electron. These are weakly attracted by the magnetic field.

Ex - O_2, Cu^{2+}, Mn^{2+}, etc

② **Dimagnetic** - This type of magnetic behaviour occurs due to the all paired electron. These are weekly repel in the Magnetic field.

Ex - Zn, Hg, cd, N_2, etc.

③ **Ferromagnetic** - This type of magnetic property occurs due to all parallel domains. These are strongly attracted in the magnetic field these are used to form magnet.

Ex - Fe, Co, Ni

④ **Ferrimagnetism** - This type of magnetic property occurs due to unequal no. of parallel & unparallel domains. These are weakly attracted in the magnetic field

Ex - Fe_3O_4
(Ferro Ferric Oxide)

⑤ **Anti Ferromagnetism** - This type of magnetic property occurs in those compound which have equal no. of parallel & antiparallel domains. Their are neither attracted nor repel in the magnetic field

Ex - MnO